from 10°·9 to −188°, thus giving the latent heat of air as 53·63. These last values come very near those found by Fenner and Richtmyer; but the results are so varied that it is clear the question of the latent heat of air of very high oxygen-concentration is one requiring further investigation.

Explosions of Mixtures of Coal-Gas and Air in a Closed Vessel.

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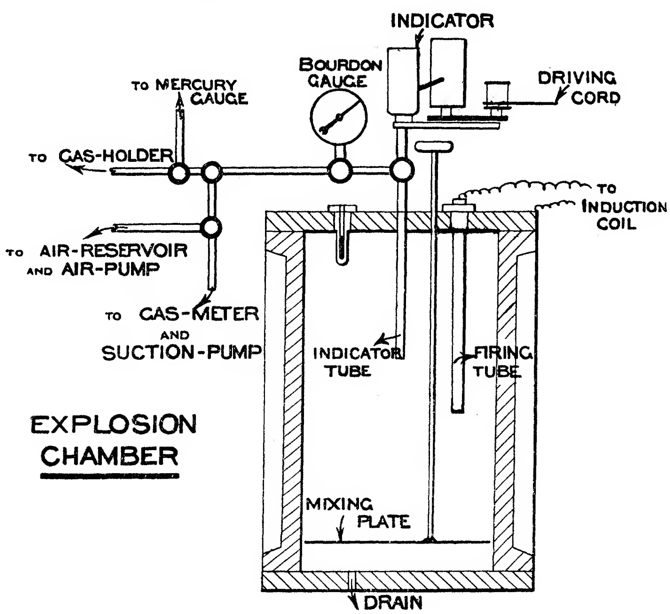
(Abstract.)

The experiments were proposed by Professor Perry, and with his sanction and encouragement extended to more than two years' continuous work. The work had for its original object the determination of the explosive properties of compressed mixtures of coal-gas and air.

The main apparatus was designed by Messrs. McDiarmid and Mann, students of the Royal College of Science, South Kensington, and was made before the authors of this paper became connected with the work.



In the preliminary experiments it was found necessary to mix the gases independently of diffusion, and most of the experiments have consequently been made at an initial pressure of 35 lbs. per square inch absolute, as this allowed a considerable volume of air to be pumped into the cylinder after the coal-gas had been admitted. Eventually it was found necessary to take still greater precautions in special cases, and mechanical mixing was resorted to.

The figure shows the explosion cylinder, which was 18 inches long and 10 inches in diameter internally. The records were taken with an ordinary indicator, the spring being usually 150 lbs. per square inch per inch. The recording drum was made to revolve continuously at a speed giving 42·5 inches of diagram per second. By varying the firing arrangements the mixtures could be ignited at different points, and a further deviation from previous work was made by altering the length of the tube which led to the indicator. The firing tube shown in the figure was closed at the top where the spark was produced, and communication with the cylinder took place through a pin-hole near the bottom. The proportion of coal-gas to air was kept constant, and using the above tube the mixture was fired at different points. In general, changes resulted both in the time of explosion and in the maximum pressure.

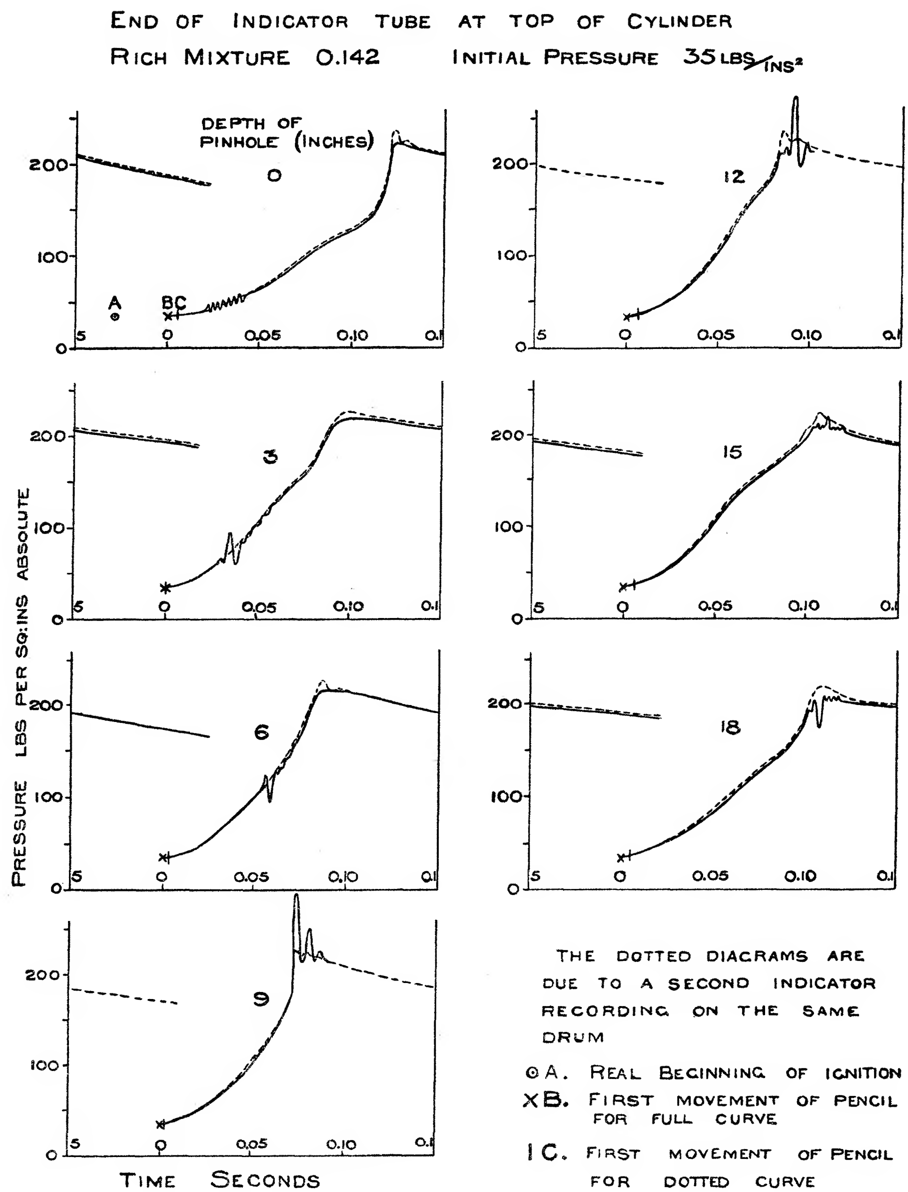
For the most explosive mixture the change in the maximum pressure was small (fig. 8 of original paper), being only of the order of 1 per cent., but in weak mixtures the variations sometimes exceeded 30 per cent. Such differences can only be observed in a vessel which absorbs heat, but it does not thereby follow that the differences are entirely due to the heat lost by the gases before the highest pressure is reached, since the maximum pressure does not coincide with the end of combustion when the rate of cooling approaches the rate of reception of heat by explosion. This and the cooling loss can be differentiated in some of the diagrams obtained, and the experiments were used as a guide to correction.

Convection currents were also indicated by the method of firing, by explosions starting at the bottom of the cylinder being quicker than an otherwise similar one beginning at the top. The currents are sometimes very considerable.

In order to reduce the cooling effects, the explosion was often commenced at four points in the axis of the cylinder. The four spark-gaps were in one continuous circuit, and the sparks, therefore, occurred simultaneously. Keeping the initial pressure constant the mixture was varied. The highest pressure and the most rapid explosion was produced when the oxygen of the air was just completely burnt. The pressure fell continuously as the pro-

portion of coal-gas to air was diminished, until the fractional volume of the mixture occupied by the coal-gas was about 1 in 12. A sudden change then

Fig. 8.



occurred, and combustion remained incomplete after explosion. Mixtures between 1 in 12 and 1 in 17 were still explosive, but the amount of gas burnt

decreased, at first suddenly and then regularly until the limit of inflammability was reached.

If then, the gases remaining in the cylinder, after an explosion of a mixture less rich in coal-gas than 1 in 12 were used instead of air in a subsequent explosion, higher pressures should result. This was observed to be the case, and with a necessary modification furnishes the explanation of the experimental results obtained by Mr. Grover in 1895.*

In the diagrams of fig. 8 ripples are shown between the beginning of explosion and the time at which the maximum is reached. It is obvious from their position that they are not due to the inertia of the indicator. With four sparks or a single spark at the top of the cylinder these occur early in the diagram, and are not usually very noticeable. When, however, the point of firing is altered, the change is accompanied by a difference in the position of the ripples. A measurement of them, when sufficiently uniform to be measured, showed that the period was independent of the pressure at which they occurred, and eventually they were traced to sound waves in the indicator tube produced by the arrival of the flame at its open end. All the observed conditions are then satisfied. Supposing then that the end of the indicator tube is in the upper surface of the cylinder (as in the cases of fig. 8), and that the mixture is fired below the middle of the cylinder, the flame will reach the bottom first and explosion will be completed when the ripples occur, that is they will occur on the top of the diagram, as in the figure. The conclusion as to their cause was confirmed by altering the length of the indicator tube and noting the change produced in the position and period of the ripples.

When the ripples occurred at the maximum pressure the amplitude was sometimes enormous, the extra pressure due to the ripples being often as great as the pressure due to combustion in the cylinder. This phenomenon is probably connected with the detonation wave investigated by MM. Mallard and Le Chatelier† and by Professor H. B. Dixon.‡ There is no evidence of the detonation wave in the cylinder itself in any of our experiments. The big movements are never found with weak mixtures, or even in rich mixtures fired with short tubes.

With weak mixtures, even when combustion is complete after explosion, the ripples indicate that the flame travels through the more inflammable portions of the mixture first, and therefore that the constituents burn

* "Modern Gas and Oil Engines," Grover.

† 'Ann. des Mines,' 1883.

‡ 'Phil. Trans.,' A, 1903.

successively. This type of combustion can be detected until the coal-gas occupies more than one-eighth of the volume of the mixture.

As explosion begins very slowly, a small amount of friction in the indicator introduced an appreciable error in the time of explosion. This was estimated by making an external gap in the spark circuit which included the indicator paper. By this means a hole was pierced in the paper at the time of sparking and (fig. 8) shows the amount of error in a particular case. (The necessary corrections are given in the full paper, which is preserved in the Archives of the Royal Society.)

Experiments on Compressed Mixtures.

These experiments form an extension of the work of Mr. D. Clerk in 1886.*

The arrangement of four sparks was found to produce the most consistent results, and it was then noticed that slight changes in the composition of the coal-gas affected the experiments, particularly the rate of cooling. To make comparative experiments, therefore, it is necessary to do them at the same time and on the same gas. Three series are given, each the result of one day's experiments. The gas used in the first two is the same, but different to that used in the third series.

Series 1 (fig. 11).

Mixture constant (volume of coal-gas divided by the volume of air = 0·168). Initial pressure varied from $\frac{1}{2}$ to 3 atmospheres.

Series 2 (fig. 12).

Mixture constant (0·105). Initial pressure as in Series 1.

Series 3 (fig. 13).

Initial pressure constant. Mixture varied.

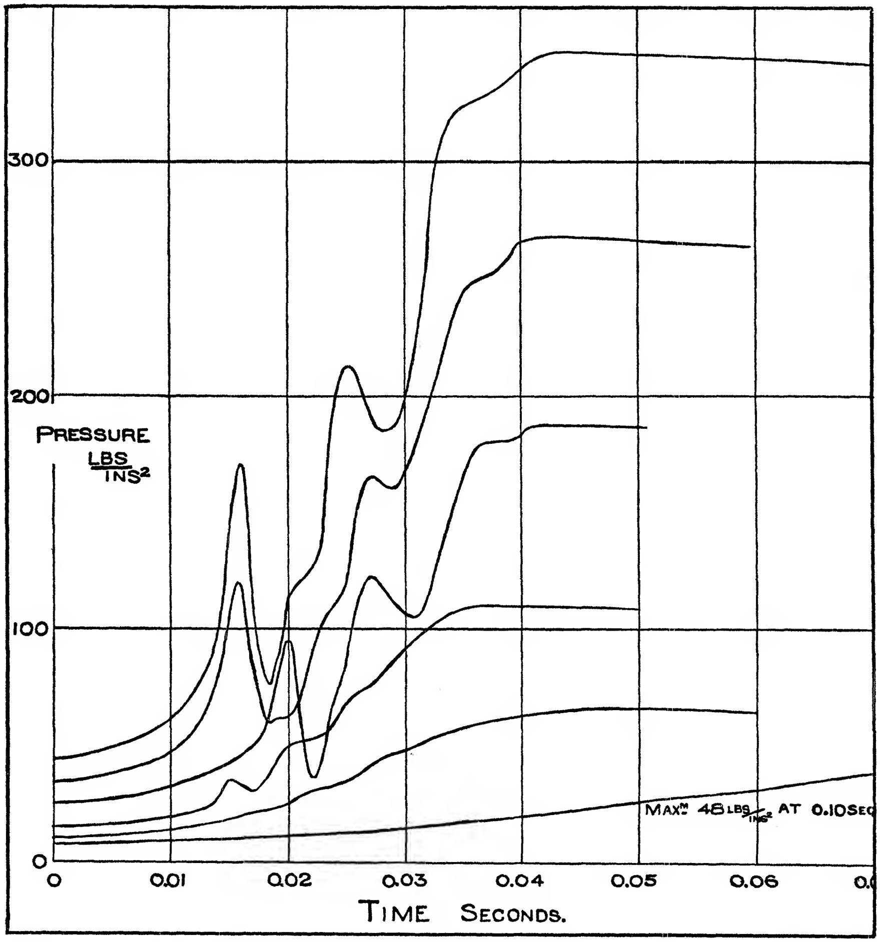
(Tables accompanying these figures are given in the full paper.)

From fig. 11 it will be seen that for a mixture of 0·168 the time of explosion is almost independent of the initial pressure between one and three atmospheres, but considerable increase is noticed for the two lower pressures. Similarly, between the same limits the ratio of the maximum to the initial pressure is constant. With the weaker mixture the time of explosion increased as the initial pressure decreased, without any decided effect on the ratio of the maximum and initial pressures (fig. 12).

The mixtures for Series 3 are such that the volumes of coal-gas burnt

* 'Proc. Inst. Civil Eng.,' 1886.

Fig. 11.



increase in arithmetical progression. These experiments show clearly that the heating value of unit volume of coal-gas increases as the mixture gets weaker (fig. 13).

Fig. 14 gives the cooling curves for the three series. By analysing the curves it will be seen that the rate of cooling increases with increase of initial pressure, but is independent of the relative proportions of coal-gas and air.

Hypotheses Introduced in the Calculation of Explosive Phenomena.

The outstanding differences between calculated and experimental results can now be explained by dissociation or an increasing specific heat. The hypothesis of a specific heat increasing with temperature is based entirely, so

Fig. 12.

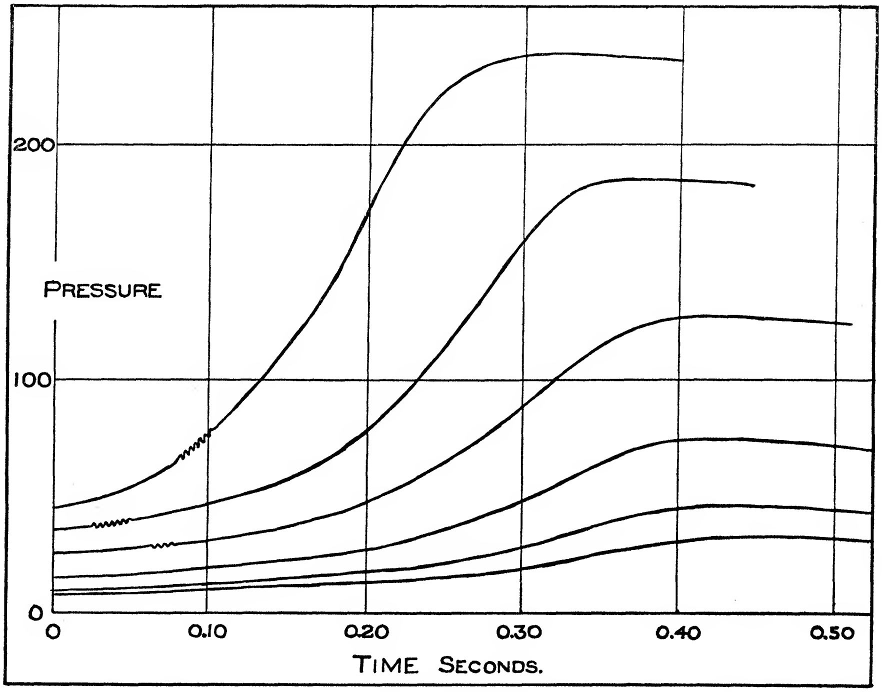
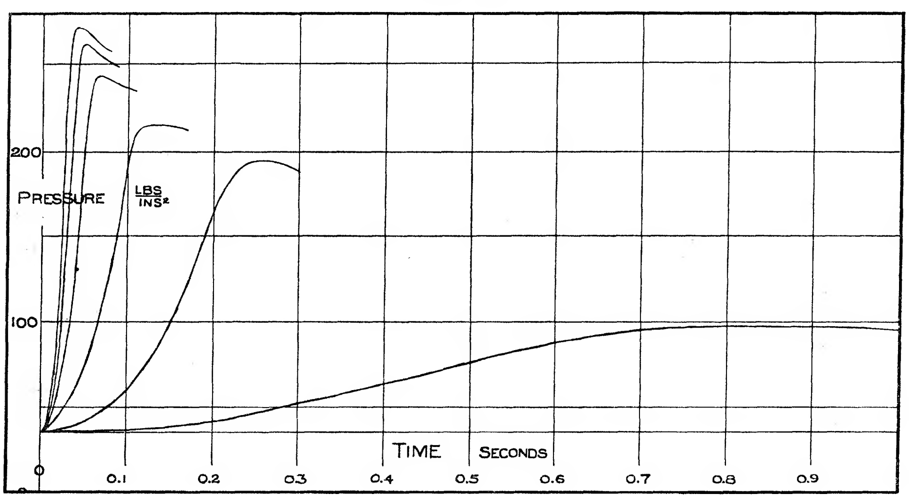
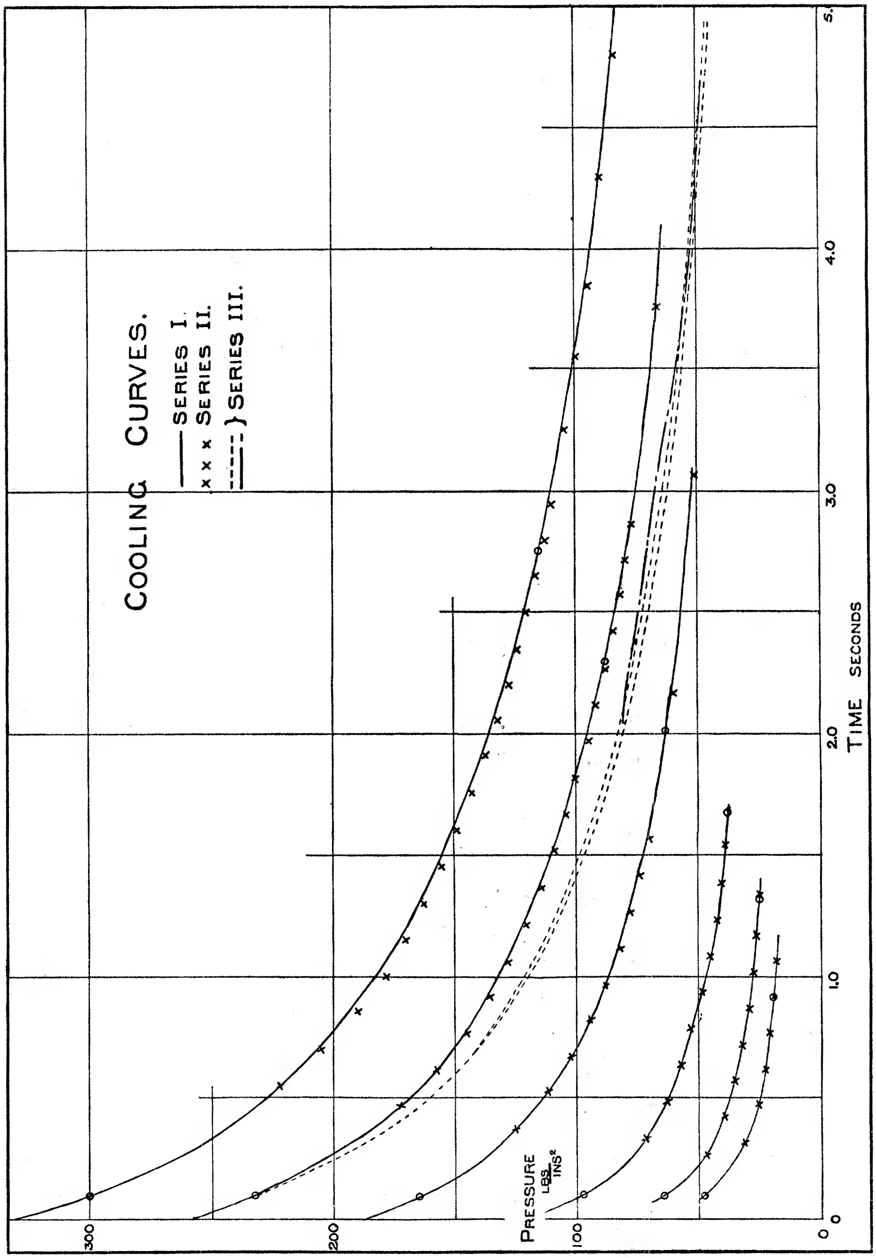


Fig. 13.



far as experimental evidence is concerned, on the work of MM. Mallard and Le Chatelier. They examined their cooling curves carefully in the search for a discontinuity at the lower limit of dissociation. Fig. 15 shows an analysis

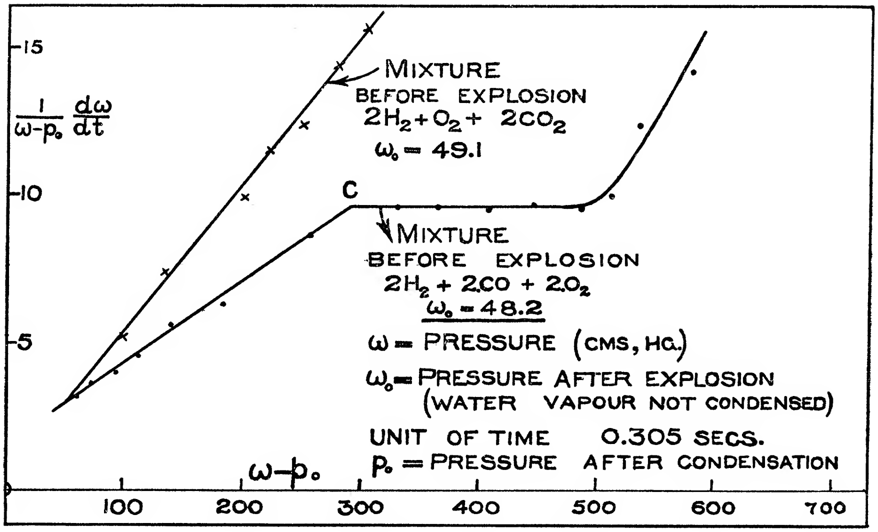
Fig. 14.



of two of their curves.* The lower curve shows the discontinuity in question at C. In both explosions concerned in diagram 15, the products are the same

* 'Ann. des Mines,' 1883.

Fig. 15.



both in composition and mass. In comparing results during cooling therefore, equal pressures mean equal temperatures. The rate of loss of pressure divided by the pressure is shown as the ordinate of the figure and the ratio of the two ordinates for any given abscissa, therefore gives the ratio of the rates of cooling in the two cases. Where $\omega - \rho_0$ is 300, the rate of cooling in one case is 50 per cent. greater than in the other.

The only apparent difference between two such cases lies in the maxima reached, and the only other experiments which afford any evidence on this point* agree in showing that the higher the maximum pressure and temperature, the lower the rate of cooling at any given subsequent temperature and pressure. The rise in the temperature of the cylinder walls would produce just such a change. A mathematical and experimental investigation showed that the metal itself does not increase in temperature greatly, and a film must therefore exist on the surface which sometimes attains a temperature of several hundred degrees Centigrade. Such a hypothesis satisfies all the observed experimental conditions, whilst it would be exceedingly difficult, if not impossible, to explain either the upper steep part of the curve in fig. 15, or the difference in the rates of cooling for the two cases, on the idea that C is the limit of dissociation.

Experiments at ordinary temperatures have not shown any such increase in specific heat as is necessary for the above hypothesis.

In order to determine the fraction of heat developed, the composition of

* 'Ann. des Mines,' 1883, p. 427.

the coal-gas and its calorific value were obtained. For the richest mixture (0·184 of coal-gas to 1 of air) the pressure obtained was 65·7 per cent. of that calculated. This fraction increased as the mixture was weakened, and was about 80 per cent. when combustion became incomplete. The highest temperature for the richest mixture is 2430° C. absolute, and the heat developed 63·2 per cent. On the hypothesis of increasing specific heat, the temperature would be 6 per cent. greater.

Summary.

Mixtures of coal-gas and air are not inflammable until the volume of coal-gas is greater than one-seventeenth of the combined volumes. Only a very small fraction of the gas then burns, the amount burnt rapidly increasing with increased richness of the mixture until the coal-gas is one-twelfth of the total volume. The least inflammable of the constituents then burns, and combustion becomes and remains complete so long as air is in excess. In these latter cases it is still probable that the constituents burn successively and not simultaneously.

The hypothesis of a specific heat increasing with temperature is not supported by direct experiment, and cannot be proved by any work on the pressures produced by explosion, the authors believing that a proof would require the measurement of temperature.

Direct experiments by Deville at temperatures below 1400° C. have shown that both steam and carbon dioxide are partially decomposed, and this dissociation is therefore taken by us as the sole explanation of the difference between the pressures calculated for explosions in a closed vessel and those actually obtained.